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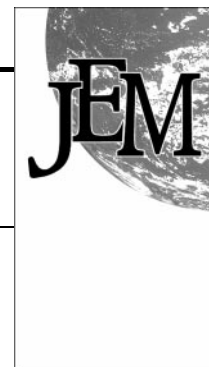
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# The determination and distribution of Zn in surface water samples collected in the northeast Atlantic Ocean†

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Dissolved Zn concentrations were determined in surface water samples collected on-line along transects in the eastern North Atlantic in spring (March 1998). Two frontal zones could be identified in the research area by a change in salinity, temperature and nutrient concentrations. One zone was identified at 42° N, separating the North Atlantic central water (NACW) and the Atlantic surface water (ASW) from each other, and another one crossing the continental slope at 12° and 8° E, respectively. Variability in Zn concentrations was observed near these zones, not only as a result of a change of water mass, but also due to external Zn sources. Surface Zn concentrations were 0.5–1 nM and 2 nM in the NACW and ASW, respectively, increasing to 4 nM over the continental shelf and finally 5–6 nM in the English Channel. Contributions of Zn derived from shelf sediments appear to be the major source for the enriched surface values in the continental zone.

## 1. Introduction

Notably the very low Zn concentrations existing in seawater and the risk of contamination have made its determination problematic. This has resulted in the availability of very few accurate Zn data in the past. However, reliable Zn data are needed to differentiate between natural processes and anthropogenic inputs. While in the open ocean Zn is strongly involved in the biological cycle, in coastal waters biogeochemical processes and external inputs regulate its concentration. Recently however, progress has been made in the accurate measurement of Zn, giving the opportunity for detailed distribution studies.<sup>1–8</sup>

From the few surface trace metal data available, some clear observations could be made. Kremling<sup>9</sup> for example, observed trace metal fronts in European shelf waters. He explained these fronts as mobilization of the trace metals from partly reduced (organic rich) sediments and a subsequent vertical mixing into the water column. Pohl *et al.*<sup>3</sup> presented trace metal data in surface waters of the North Atlantic, including Zn, and observed an increase in Zn concentration from about 0.5 to 1.5 nM passing the west European shelf, confirming the observation made by Kremling<sup>9</sup> for other metals. In the northern North Sea, Nolting *et al.*<sup>8</sup> were among the first to report relatively low dissolved Zn concentrations of around 3 nM in the surface waters of this shelf sea.

Dissolved Zn concentrations in seawater have usually been determined in our laboratory by APDC/DDDC pre-concentration using organic solvent extraction<sup>10</sup> followed by graphite furnace atomic absorption spectrometry.<sup>11</sup> A disadvantage of this technique is its unsuitability for immediate shipboard Zn measurements. Samples can be extracted on-board ship in a clean air container, but analysis has to be done in the laboratory. Nowadays, the increased understanding of Zn behaviour in marine systems requires methods that can be performed directly at sea. This can be fulfilled with continuous underway sampling and flow injection analysis with fluorescence (FIA-FL) detection, as developed by Nowicki *et al.*<sup>12</sup>

Here we report the results of dissolved Zn distributions in

surface waters obtained during a cruise in the northeast Atlantic Ocean including the English Channel. The procedure and methods used are especially useful for sampling with high resolution and for monitoring of trace metals in the marine environment.

## 2. Sampling and methods

### 2.1. Surface seawater sampling

Surface samples were collected in the northeast Atlantic Ocean during a cruise with R.V. Pelagia from the 2nd to 27th March 1998. The research area was situated between 37° and 47° N and 23° and 0° W. The station positions ( $n = 154$ ) are presented in Fig. 1, and are divided into four different transects. Transect one (I) started outside the English Channel on the ridge of the continental slope, extended southwards until 38° N, 23° W, and covers samples 1–40. The second transect (II–VI) is a compilation of different tracks, sailing several times north

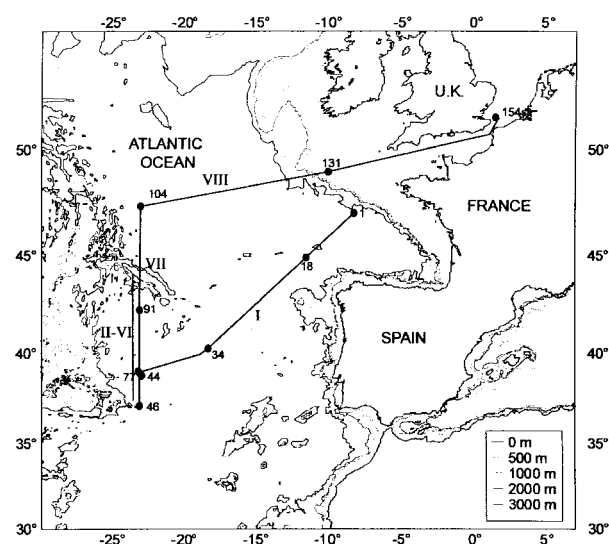


Fig. 1 Map of the research area with station numbers and the different transects I–VIII.

†Presented at QUASIMEME–QUASH 1999, Egmond aan Zee, The Netherlands, October 6–9, 1999.

and south along the 23° W longitude, and covers samples 41–76. The third transect (numbered VII) is a south–north survey along the 23° W meridian (samples 77–103), and the fourth transect (numbered VIII) is a west–east survey, through the English Channel ending in the southern North Sea, samples 104–154.

Samples were collected every hour, from continuously pumped seawater through a PVC tube connected to a towing fish, while the ship was sailing at 8 knots. Contamination from the ships hull was avoided by towing the fish attached to a hydrographic ‘A’ frame at a distance of ~5 m and at a depth of 3 m from the ship. The tubing had been cleaned extensively by 1 M HCl, rinsed with deionized (DI) water, and before actual sampling the seawater had been pumped through the tube for at least half an hour. We used a Cole-Parmer Masterflex I/P variable speed modular pump drive model 7591-1-00 with an Easy-Load model 7529-00 pump head with silicone tubing.<sup>13</sup> In the shipboard clean laboratory van the samples were filtered in-line through a Sartorius Sartobran filter cartridge (0.2 µm) at a flow rate of ~1 l min<sup>-1</sup>, and collected in 50 ml polyethylene sampling bottles. Seawater was continuously pumped through the tube, but when no sampling was performed it was run through a by-pass to avoid clogging of the cartridge by suspended particles. Sampling bottles had been cleaned intensively by rinsing them with hot (60 °C) 6 M HCl for at least 24 h, followed by ample rinsing with DI water. After collection the samples were acidified to pH 1.9 with 50 µl triple quartz distilled (3QD) concentrated nitric acid within a class 100 laminar flow hood. To check the reliability of the towing fish sampling method, a comparison by simultaneous sampling from a zodiac and from the towing fish was performed during a 1 h mini-transect (5 samples). No significant differences in zinc concentrations could be detected between the two sampling techniques.

## 2.2. Methods

All precautions to avoid contamination were taken and the bottles, tubing and instrumentation were carefully cleaned before use. Sample handling and sample intake were contained within a class 100 laminar flow hood.

Simultaneously with the samples collected for Zn analysis, bottles were filled for phosphate, silicate and nitrate determinations. These major nutrient were determined by TRAACS 800 auto analysers.<sup>14</sup> Detection limits were 0.02 µM for phosphate, 0.02 µM for nitrate and 0.1 µM for silicate.

Surface temperature, salinity and fluorescence were continuously measured from the ships water inlet with an Aqua-Flow. Water was collected from 3 m below the surface, the temperature was measured and the water was pumped into the Aqua-Flow were the conductivity and the temperature were measured. From these parameters the salinity was calculated. On every expedition the Aqua-Flow was controlled by collecting samples which were measured at NIOZ with a salinometer and when necessary corrections made.

Total dissolved Zn was determined by flow injection analysis (FIA) followed by fluorimetric detection.<sup>12</sup> Before starting the analyses, 0.3 ml of an ammonium acetate buffer (Suprapur) was added to the acidified samples to bring the pH to 4.5–5.0. In short, the method is as follows: first, the column, containing 8-hydroxyquinoline (8-HQ) immobilized on Fractogel, was washed with strong acid (1 M HCl). This was followed by a sample loading period during which the Zn was accumulated onto the column. After a rinse with DI water the Zn was eluted from the column with 0.08 M HCl and mixed with a sodium tetraborate buffered *p*-tosyl-8-aminoquinoline (pTAQ) solution in the reagent stream. After complexation the sample was sent through a 16 µl quartz flow-through cuvette, and the fluorescence was measured in a Waters 470 scanning fluorescence spectrophotometer and recorded on a chart recorder, set

at 5 mV. The fluorimeter settings were as follows: excitation wavelength 377 nm; emission wavelength 495 nm; excitation and emission slits 5 nm. Reagents were prepared fresh each day and we used Suprapur HCl as carrier acid. Timing parameters were as follows: load time 120 s, rinse time 120 s and injection time 100 s. The method was completely computer-controlled, and 10 samples could be measured in one run. A proportion of the surface samples were directly measured on-board, the remainder were analyzed at the home laboratory.

Accuracy, precision and sensitivity were checked every day by a four-point standard addition to a low Zn containing reference bulk seawater (Atlantic Ocean water), yielding linear calibrations, and independent validation *versus* a certified reference material seawater NASS-5 (National Research Council of Canada). Typical additions were: +0, +2.29, +4.58, +6.87 and +9.16 nM Zn. In this way we measured 20 calibration lines in the bulk seawater during the analysis period and calculated a mean Zn value of  $2.36 \pm 0.32$  nM (relative standard deviation (RSD)=13.7%), (not blank corrected), which gave a relative error of  $\pm 13.7\%$  (Table 1). A mean slope of 1.72 with a variation of 22.6% was calculated, which makes it very important to make a calibration every day before starting the measurements. For accuracy checks, the reference seawater NASS-5 was regularly measured together with the samples. Over a time period of one month this reference sample was measured 13 times and the results ( $1.87 \pm 0.20$  nM,  $n = 13$ ) were in good agreement with the certified value ( $1.56 \pm 0.56$  nM). Our values were not corrected for any possible Cd interference ( $\leq 10\%$ ), as reported by Nowicki *et al.*,<sup>12</sup> which may have resulted in an overestimation in our results. We also participated in the QUASIMEME Round 9 “Trace metals in seawater performance studies”, with the same method as described above. Our results were within 5% of the assigned values. Blanks were measured as suggested by Nowicki *et al.*,<sup>12</sup> and ranged between 0.50 and 0.95 nM over the working period. As noted by Nowicki *et al.*,<sup>12</sup> the blank is significant, but our blank was lower than the blanks they reported (1.5–3.0 nM). Possible sources for this blank value could have been an undetectable pH shift, a change in flow, or a pressure change due to valve rotation.<sup>12</sup> It was noticed that even using the cleanest DI water as sample, a very small but reproducible signal was introduced by instrumental sources, that could not

**Table 1** Daily prepared calibration lines for the Zn determination with a standard seawater, measured over a time period of six weeks<sup>a</sup>

Date	<i>a</i>	<i>b</i>	<i>c</i>	<i>r</i>
20 Oct	0.694	1.215	2.09	0.9870
21 Oct	0.701	1.690	2.43	0.9991
22 Oct	0.710	1.650	2.25	0.9995
25 Oct	0.910	1.870	2.03	0.9995
26 Oct	0.873	2.000	2.18	0.9996
27 Oct	0.928	2.010	2.21	0.9999
28 Oct	0.886	1.850	2.37	0.9942
29 Oct	0.753	2.650	1.93	0.9997
09 Nov	0.714	1.450	2.38	0.9985
10 Nov	0.715	2.208	3.08	1.0000
11 Nov	0.686	1.860	2.77	0.9999
12 Nov	0.812	1.440	1.85	0.9998
15 Nov	0.594	1.600	2.69	0.9993
16 Nov	0.651	1.770	2.69	0.9993
19 Nov	0.557	1.320	2.42	0.9992
23 Nov	0.707	1.740	2.40	0.9999
24 Nov	0.795	1.470	1.89	0.9998
25 Nov	0.710	1.850	2.67	0.9993
26 Nov	0.758	1.660	2.24	0.9997
29 Nov	0.773	2.085	2.58	0.9994
Mean	0.75	1.72	2.36	1.00
<i>s</i> ± 1	0.10	0.39	0.32	0.00
RSD (%)	13.25	22.60	13.72	0.30

<sup>a</sup>Concentration (*c*) = *ax* + *b*. Regression = *r*.

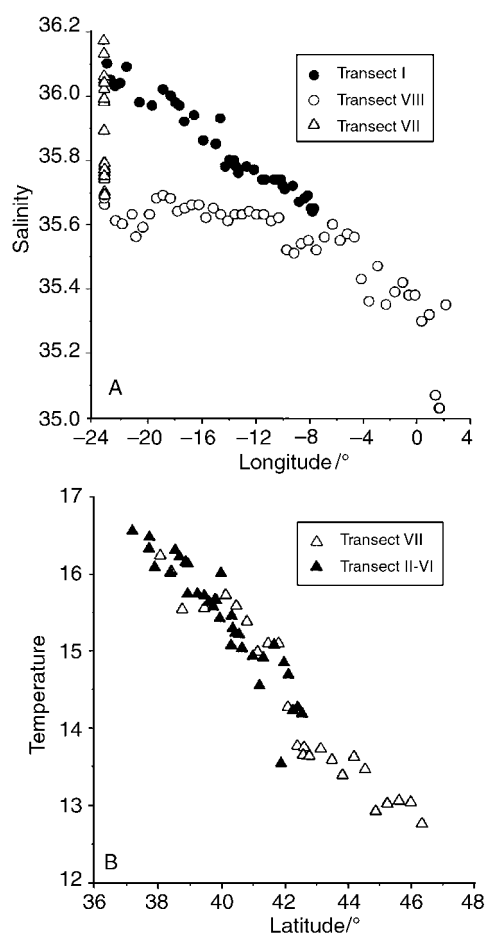
be removed. Consequently the instrumental background signal was measured regularly and corrected for. Thus, all samples were blank-corrected, but without a direct correction for a possible but maybe negligible Cd interference.<sup>12</sup>

After further experiments it appears that the origin of the blank was a fake signal from a salt effect on the column. The salt matrix of seawater affects the density of the column, causing back-pressure, which is also visible as a slight shortening of the column material, about 5% of the column length. This back-pressure resulted in a false peak equivalent to a signal of about 0.7 nM Zn. We corrected our values with the mean of the blank range, *i.e.*, 0.7 nM. After the new information concerning the blank problem this is maybe too low and the upper part of the range should have been used, *i.e.*, 0.95 or 1.00 nM. This implies that the reported surface values “maybe” have to be corrected by another 0.3 nM. For the interpretation of the observed trends this has no influence, but has consequences for the lowest Zn concentrations. If these values have to be corrected by another 0.3 nM they are comparable to the values measured by Ellwood and van den Berg.<sup>15</sup>

### 3. Results and discussion

#### 3.1. Hydrography and nutrients

Along transect I salinity increased linearly from 35.6 to 35.8, indicative of NACW (Fig. 2A),<sup>16</sup> which indicated conservative mixing between the water masses leaving the English Channel and those of the Atlantic Ocean. At salinity 35.8 a front situated at 14° W and 42° N was observed from where salinity gradually increased from 35.9 to 36.2, representative of ASW.<sup>17</sup> In contrast to transect I no strong salinity gradient was observed along transect VIII. Salinity remained constant at



**Fig. 2** Salinity against longitude for transects I, VII and VIII (A) and temperature against latitude for transects VII and II–VI (B).

35.6–35.7 until passing the continental slope at 10° W, where a dip in salinity to 35.5 occurred. From here on it increased again to 35.6, and at 4° W sailing into the English Channel salinity decreased gradually to 35.3. By plotting salinity against latitude, the frontal zone at 42° N as observed in transect I, was confirmed by the change in salinity at transect VII.

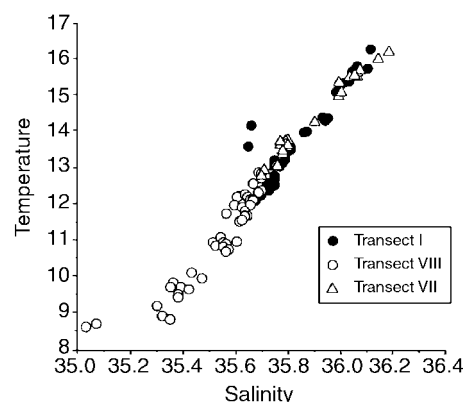
The separation between the different water masses was confirmed within the temperature pattern, which increased from 12.0 to 16.3 °C along transect I. In the gyre, the temperature was between 11.6 and 13.6 °C, while this dropped to 8.8 °C in the English Channel (Fig. 2B). The homogeneous mixing of the different water bodies is reflected in the salinity temperature plot (Fig. 3). This indicated the presence of three water bodies, NACW, ASW and the English Channel, with several fronts.

Silicate concentrations were higher in the northern part of the research area ~3 μM compared to the ~1 μM found in the southern part. The boundary between the different water masses as discussed above is clearly indicated by the silicate increase at 42° N (Fig. 4A) as also seen by the other nutrients. Nitrate and phosphate concentrations in the northern part of the research area were around 6–7 μM and 0.4–0.5 μM, respectively, and almost depleted in the southern part where plankton blooms were developing (Fig. 4B,C). Nutrient concentration decreased in the direction of the English Channel.

#### 3.2. Zinc distributions

Zinc concentrations from all surface stations are plotted against longitude and are shown in Fig. 5A. The highest Zn concentrations were detected in the coastal waters, the English Channel and southern North Sea, and ranged from 3.5 to 5.9 nM. In both transect I and VIII the Zn concentrations had a similar distribution pattern, with increasing values near the continental shelf. These increases were very pronounced and were situated in transect I at 14° W and in transect VIII at 10° W, just where the continental shelf begins. Away from the continental shelf, Zn concentrations were lower at around 1 nM, with only small variations in transect VIII. The higher Zn values measured in the outflow of the English Channel water were traceable until 12° N in transect I. Zinc concentrations measured along transect VII and during the north and south tracks (II–VI) were of the same order as those found at the arriving and departing transects. Besides the frontal zone observed near the continental slope, a second boundary, as indicated by salinity, temperature and nutrients at 42° N, showed a shift in the Zn concentration from 1 nM to 1.8 nM at higher latitude (Fig. 5B).

Surface distributions of Zn were more or less determined by the three areas described above with, however, local differences (Fig. 6). For instance, below the 42° N latitude at transects I and VII, with a salinity between 35.8 and 36.2, Zn concentrations increased towards the coast to 2 nM, in contrast to concentrations measured more offshore, ~1 nM. The same



**Fig. 3** Temperature against salinity for transects I, VII and VIII.



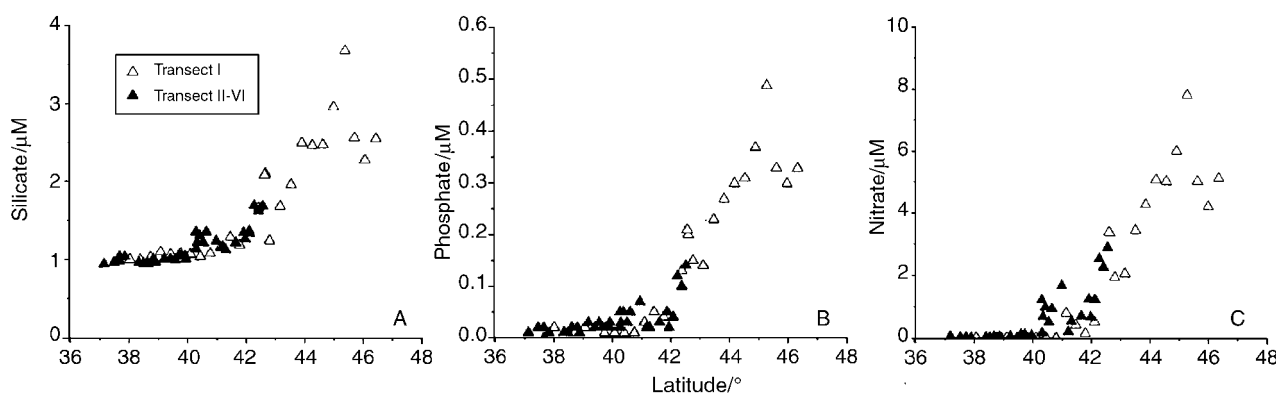


Fig. 4 Silicate (A), phosphate (B) and nitrate (C) ( $\mu\text{M}$ ) against latitude for transects VII and II–VI indicating the frontal zone at  $42^\circ$ .

gradient was observed above the  $42^\circ$  N latitude, where at salinity 35.7 and 35.8 roughly between  $42^\circ$  N and  $45^\circ$  N, Zn concentrations differed significantly. Offshore concentrations were between 1 and 2 nM, while the inshore concentrations were between 3 and 4 nM. Because the differences in concentration occurred at the same salinity this coastward increase must be ascribed to external Zn sources. The same observations have been reported for Spanish coastal waters, where an order of magnitude higher Zn concentration was measured than for Atlantic sub-surface water with the same salinity.<sup>17</sup> If the Zn distributions were a result of pure mixing of two end members with different salinity and Zn concentration, a straight mixing line would be obtained. From Fig. 6 it is clear that this is not the case, values above as well as below the mixing curve were detected. Balls<sup>18</sup> used a method to calculate source concentrations to explain trace metal concentrations in Scottish coastal waters. Using this method to calculate end member concentrations, with 1 nM Zn at a salinity of 36.1 as one end member and 4 nM at 35.3 in the English Channel as an

intermediate, a zero salinity Zn concentration of 130–140 nM is calculated. This value is very realistic taking into account the dissolved Zn values reported for rivers flowing into the English Channel, which range from 15 to 900 nM.<sup>5</sup> The Zn value of 150 nM reported for the river Seine, is in good agreement with the value calculated from our mixing line.<sup>19</sup> On the other hand, the Zn concentrations of 20 nM measured in the river Gironde<sup>20</sup> are lower and would have minor influence on the Zn values found in the research area. Dissolved Zn concentrations ranging between 5 and 20 nM have been reported for English Channel coastal waters.<sup>21</sup> These values are significantly higher than the ones we have measured. In fact the majority of the Zn data reported<sup>21</sup> for English coastal waters were more in the upper part of the range than in the lower part. This would imply that our calculations, with the 4 nM Zn measured in this study for Channel water, are probably an underestimation of the real fresh water end members.

In summary, we can conclude that part of the observed Zn concentrations can be explained by river inputs, but that other sources, for instance, sediment,<sup>9</sup> are responsible for the higher Zn values observed near the continental shelf. However, despite the very consistent Zn distributions measured in the open northeast Atlantic, atmospheric inputs could not be excluded but are of minor importance in the English Channel.

#### 4. Conclusions

With the method described here, it is possible to collect on-line surface seawater samples with high resolution. The sampling procedure has proven to be contamination-free for trace metals. This has labor and time saving advantages and because results are directly available on-board ship, trends and inadvertent contamination sources can easily be detected and remedied.

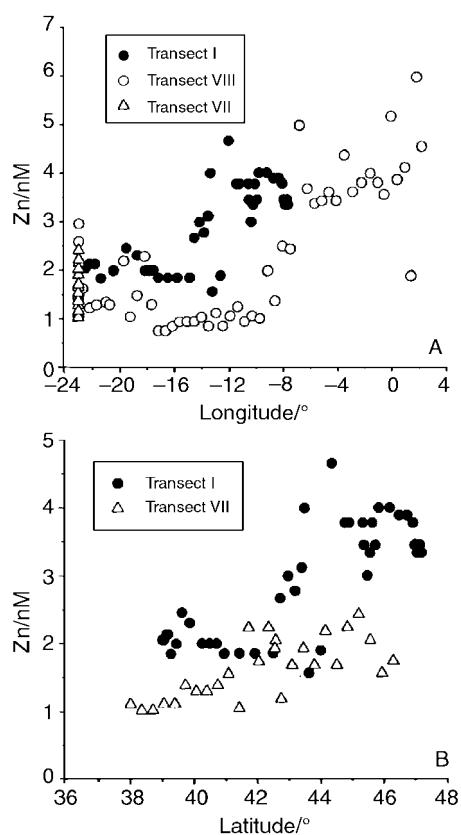


Fig. 5 Concentration of dissolved Zn (nM) against longitude (A) and latitude (B) for the different transects indicating the shift in concentration at the frontal zones.

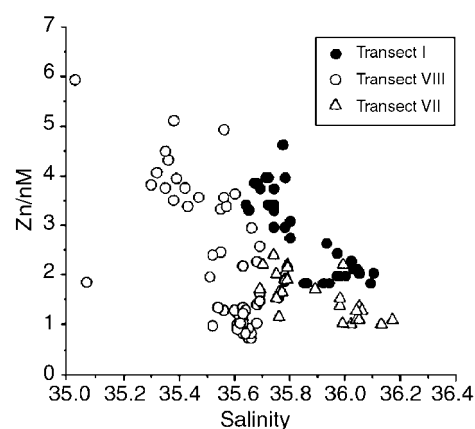


Fig. 6 Dissolved Zn concentration against salinity for the different transects. At the same salinity different Zn concentrations were detected as an indication for different external Zn sources.

The salt matrix of the seawater affects the density of the column, causing back-pressure. This resulted in a significant blank signal and, especially when low concentrations have to be measured, one should be aware of this problem.

Dissolved Zn concentrations in the surface water in the eastern part of the open North Atlantic are low and vary between 0.5 and 2 nM, with increasing concentrations near shore and in the English Channel. The distribution of dissolved Zn in the northeast Atlantic Ocean is regulated by frontal zones and external inputs near the continental shelf.

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